# PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-087812
(43)Date of publication of application : 27.03.2002

(51)Int.Cl. C01B 37/02
G02B 27/28

(21)Application number : 2000-283100
(22)Date of filing : 19.09.2000

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## (54) PATTERNED SILICA MESO-STRUCTURE THIN FILM, MESO POROUS SILICA THIN FILM AND MANUFACTURING METHOD THEREOF

(57)Abstract:
PROBLEM TO BE SOLVED: To provide an optionally shaped silica meso-structure thin film having a uniaxial oriented fine pore structure in an optional direction at an optional position of a substrate in an optional direction.
SOLUTION: The patterned silica meso-structure thin film is a silica meso- structure thin film arranged at the optional position on a high molecular compound thin film formed on the substrate and has the uniaxially oriented fine pore structure, in which the orientation direction of the tubular fine pores in the thin film is arranged in the uniaxial direction, the thin film is patterned into a required shape and the orientation direction of the fine pores in at least 1 region in a plurality of regions of the patterned thin film is different from others.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

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CLAIMS

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[Claim(s)]
[Claim 1] It is the silica meso structure thin film arranged in the location of the arbitration on the high-molecular-compound thin film formed on the substrate. While the direction of orientation of the pore of the shape of tubing in this thin film is equal to 1 shaft orientations, patterning of this thin film is carried out to the desired configuration. And the silica meso structure thin film which has the pore structure of the uniaxial orientation nature characterized by the directions of orientation of the pore of at least one or more fields of two or more fields of this thin film by which patterning was carried out differing and by which patterning was carried out.
[Claim 2] The silica meso structure thin film which has the pore structure of uniaxial orientation nature according to claim 1 where the high molecular compound formed on the substrate is characterized by including two or more continuous methylene groups in a repeat structural unit and by which patterning was carried out.
[Claim 3] The meso porous silica thin film which has the pore structure of the uniaxial orientation nature characterized by removing the surfactant in pore from a silica meso structure thin film according to claim 1 or 2 and by which patterning was carried out.
[Claim 4] The meso porous silica thin film which has the pore structure of uniaxial orientation nature according to claim 3 where the method of removing said surfactant is baking and by which patterning was carried out.
[Claim 5] The meso porous silica thin film which has the pore structure of uniaxial orientation nature according to claim 3 where the method of removing said surfactant is the extract by the organic solvent and by which patterning was carried out.
[Claim 6] The process which forms a high molecular compound thin film in a substrate front face, and the process which gives the orientation restraining force of the direction of arbitration to two or more fields of the arbitration of this high molecular compound thin film using the mask rubbing method, The process which creates the thin film of the silica meso structure by which said substrate which performed rubbing processing was held in the acid surfactant water solution containing a silicon alkoxide, and the direction of pore was controlled on this substrate, The manufacture approach of the silica meso structure thin film by which patterning was carried out of having the pore structure of the uniaxial orientation nature characterized by including the process which fabricates this silica meso structure thin film in the configuration of arbitration with ultra-fine processing technology in the location of the arbitration on a substrate.
[Claim 7] The manufacture approach of the silica meso structure thin film [ PATANIGU / thin film ] of having the pore structure of uniaxial orientation nature according to claim 6 where said ultra-fine processing technology uses a lithography technique.
[Claim 8] The manufacture approach of the silica meso structure thin film by which patterning was carried out of having the pore structure of uniaxial orientation nature according to claim 6 where said ultra-fine processing technology uses a focusing ion beam machining technique.
[Claim 9] The manufacture approach of the silica meso structure thin film by which patterning was carried out of having the pore structure of uniaxial orientation nature according to claim 6 where the high molecular compound formed on the substrate is characterized by including two or more continuous methylene groups in a repeat structural unit.

[Claim 10] The process which forms a high molecular compound thin film in a substrate front face, and the process which gives the orientation restraining force of the direction of arbitration to two or more fields of the arbitration of this high molecular compound thin film using the mask rubbing method, The process which creates the thin film of the silica meso structure by which said substrate which performed rubbing processing was held in the acid surfactant water solution containing a silicon alkoxide, and the direction of pore was controlled on this substrate, The process which fabricates this silica meso structure thin film in the configuration of arbitration with ultra-fine processing technology in the location of the arbitration on a substrate, The manufacture approach of the meso porous silica thin film by which patterning was carried out of having the pore structure of the uniaxial orientation nature characterized by including the process which removes a surfactant out of the silica meso structure thin film formed on the substrate.

[Claim 11] The manufacture approach of the meso porous silica thin film by which patterning was carried out of having the pore structure of uniaxial orientation nature according to claim 10 where said ultra-fine processing technology uses a lithography technique.

[Claim 12] The manufacture approach of the meso porous silica thin film by which patterning was carried out of having the pore structure of uniaxial orientation nature according to claim 10 where said ultra-fine processing technology uses a focusing ion beam machining technique.

[Claim 13] The manufacture approach of the meso porous silica thin film by which patterning was carried out of having the pore structure of uniaxial orientation nature according to claim 10 where the method of removing said surfactant is baking.

[Claim 14] The manufacture approach of the meso porous silica thin film by which patterning was carried out of having the pore structure of uniaxial orientation nature according to claim 10 where the method of removing said surfactant is the extract by the organic solvent.

[Claim 15] The manufacture approach of the meso porous silica thin film by which patterning was carried out of having the pore structure of uniaxial orientation nature according to claim 10 where the high molecular compound formed on said substrate is characterized by including two or more continuous methylene groups in a repeat structural unit.

[Claim 16] The polarization modulation element which can generate the polarization modulated by vibration of the optical exposure and substrate using this thin film that is a meso porous silica thin film which has the pore structure of uniaxial orientation nature which is different to the field to which each other is adjoined on a substrate, and by which patterning was carried out, and introduced the molecule which emits light by excitation by optical exposure into this pore structure.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the technique which carries out patterning of the thin film of the silica meso structure by which the direction of orientation of tubular pore was controlled towards desired in more detail to a desired configuration in the location of the request on a substrate in relation to the application to functional devices used [ especially ] for a catalyst, an adsorbent, etc., such as an optical element of an inorganic oxide porous body, about the silica meso structure thin film by which patterning was carried out, a meso porous silica thin film, and its manufacture approach.
[0002]
[Description of the Prior Art] As an approach of depositing the meso porous structure thin film which has the pore structure of uniaxial orientation nature on a substrate for example, "Journal of the American Chemical Society" -- the 121st volume The approach which used for the substrate Si (110) which is indicated by 7618 pages, "Nature" -- the approach and "Science" which used for the substrate the 379th volume and graphite (Graphite) which is indicated by 703 pages -- there is an approach which used for the substrate the 273rd volume and a mica (Mica) which is indicated by 892 pages.
[0003] There is the approach of carrying out patterning of the silica meso structure thin film easily using the 287th volume of "Science" and software lithography which is indicated by 465 pages as an approach of carrying out patterning of the silica meso structure thin film to the configuration of arbitration.
[0004] as the approach of creating the meso porous structure which had uniaxial orientation nature in the direction of arbitration -- "Science" -- there is the formation approach of the meso porous structure which has the pore structure of uniaxial orientation nature using the 288th volume and a magnetic field which is indicated by 652 pages. furthermore -- as the formation approach of the meso porous structure which has the pore structure of uniaxial orientation nature in the direction of the arbitration of the location of the arbitration on a substrate -- "Nature" -- there is the approach of forming a micro capillary in the direction of the arbitration of the location of the arbitration on the 390th volume and a substrate which is indicated by 674 pages, and forming the meso porous structure which carried out uniaxial orientation in the direction by impressing electric field in the direction of a capillary.
[0005]
[Problem(s) to be Solved by the Invention] However, in order to have applied to the functional device in addition to this, the technique which forms an optical element, such as performing polarization control of photoluminescence as hosts, such as a conductive polymer, using the meso porous structure with uniaxial orientation nature, and the meso porous structure thin film to which the direction of meso pore was equal in an arbitration configuration in the direction of arbitration is important for the location of the arbitration on a substrate, and the following troubles were in the Prior art in it.
[0006] By the approach of depositing on substrates, such as Si (110), the substrate dependency of the film formed is large, and is restricted to the substrate with the order nature in atomic level, and a problem is in the arbitration controllability of the direction of meso pore within the same substrate further. Moreover, by the approach of carrying out patterning of the silica meso structure easily using software lithography, a silica meso structure thin film with uniaxial orientation nature cannot be created.
[0007] And by the formation approach with the pore structure of the uniaxial orientation nature by the

magnetic field of the meso porous structure, in order to generate a strong magnetic field, equipment became large-scale, and the problem was in the limit to the magnitude of a substrate, or the formation in the location of arbitration. Furthermore, by the formation approach of the meso porous structure which has uniaxial orientation nature using a micro capillary, production of a thin film patterning was carried out [ production ] to the configuration of arbitration by use of a micro capillary was difficult, and there was a trouble that a creation process was still more complicated.

[0008] For this reason, the uniaxial orientation nature of this thin film by which carried out patterning of the silica meso structure thin film which has uniaxial orientation nature to the configuration of arbitration on the substrate of arbitration to the application to the functional device of a silica meso structure thin film, and patterning was carried out separately was wanted to control in the direction of arbitration.

[0009] This invention was made in view of the above-mentioned trouble, and offers the silica meso structure thin film, the meso porous silica thin film, and its manufacture approach of a configuration of the arbitration which has the pore structure of uniaxial orientation nature in the direction of arbitration in the location of the arbitration on a substrate.

[0010]

[Means for Solving the Problem] Namely, invention of the first of this invention is a silica meso structure thin film arranged in the location of the arbitration on the high-molecular-compound thin film formed on the substrate. While the direction of orientation of the pore of the shape of tubing in this thin film is equal to 1 shaft orientations, patterning of this thin film is carried out to the desired configuration. And it is the silica meso structure thin film which has the pore structure of the uniaxial orientation nature characterized by the directions of orientation of the pore of at least one or more fields of two or more fields of this thin film by which patterning was carried out differing and by which patterning was carried out.

[0011] Invention of the second of this invention is a meso porous silica thin film which has the pore structure of the uniaxial orientation nature characterized by removing the surfactant in pore from the above-mentioned silica meso structure thin film and by which patterning was carried out.

[0012] The process at which invention of the third of this invention forms a high-molecular-compound thin film in a substrate front face, The process which gives the orientation restraining force of the direction of arbitration to two or more fields of the arbitration of this high-molecular-compound thin film using the mask rubbing method, The process which creates the thin film of the silica meso structure by which said substrate which performed rubbing processing was held in the acid surfactant water solution containing a silicon alkoxide, and the direction of pore was controlled on this substrate, It is the manufacture approach of the silica meso structure thin film by which patterning was carried out of having the pore structure of the uniaxial orientation nature characterized by including the process which fabricates this silica meso structure thin film in the configuration of arbitration with ultra-fine processing technology in the location of the arbitration on a substrate.

[0013] The process at which invention of the fourth of this invention forms a high-molecular-compound thin film in a substrate front face, The process which gives the orientation restraining force of the direction of arbitration to two or more fields of the arbitration of this high-molecular-compound thin film using the mask rubbing method, The process which creates the thin film of the silica meso structure by which said substrate which performed rubbing processing was held in the acid surfactant water solution containing a silicon alkoxide, and the direction of pore was controlled on this substrate, The process which fabricates this silica meso structure thin film in the configuration of arbitration with ultra-fine processing technology in the location of the arbitration on a substrate, It is the manufacture approach of the meso porous silica thin film by which patterning was carried out of having the pore structure of the uniaxial orientation nature characterized by including the process which removes a surfactant out of the silica meso structure thin film formed on the substrate.

[0014] Invention of the fifth of this invention is a meso porous silica thin film which has the pore structure of uniaxial orientation nature which is different to the field to which each other is adjoined on a substrate and by which patterning was carried out, and is the polarization modulation element which can generate the polarization modulated by vibration of the optical exposure and substrate using this thin film that introduced the molecule which emits light by excitation by optical exposure into this pore structure.

[0015]

[Embodiment of the Invention] The silica meso structure thin film of this invention is a silica meso structure thin film arranged in the location of the arbitration on the high-molecular-compound thin film formed on the substrate. The direction of orientation of the pore of the shape of tubing in this thin film is the silica meso structure thin film which is equal to 1 shaft orientations. It is the silica meso structure thin film which has the pore structure of the uniaxial orientation nature characterized by the directions of orientation of the pore of at least one or more fields of two or more fields of this thin film by which patterning of this thin film is furthermore carried out to the desired configuration, and patterning was carried out differing.
[0016]

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## TECHNICAL FIELD

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[Field of the Invention] This invention relates to the technique which carries out patterning of the thin film of the silica meso structure by which the direction of orientation of tubular pore was controlled towards desired in more detail to a desired configuration in the location of the request on a substrate in relation to the application to functional devices used [ especially ] for a catalyst, an adsorbent, etc., such as an optical element of an inorganic oxide porous body, about the silica meso structure thin film by which patterning was carried out, a meso porous silica thin film, and its manufacture approach.

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PRIOR ART

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[Description of the Prior Art] As the approach of depositing the meso porous structure thin film which has the pore structure of uniaxial orientation nature on a substrate, for example, "Journal of the American Chemical Society" -- the approach and "Nature" which used for the substrate the 121st volume and Si (110) which is indicated by 7618 pages -- the approach and "Science" which used for the substrate the 379th volume and graphite (Graphite) which is indicated by 703 pages -- there is an approach which used for the substrate the 273rd volume and a mica (Mica) which be indicated by 892 pages.
[0003] There is the approach of carrying out patterning of the silica meso structure thin film easily using the 287th volume of "Science" and software lithography which is indicated by 465 pages as an approach of carrying out patterning of the silica meso structure thin film to the configuration of arbitration.
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EFFECT OF THE INVENTION

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[Effect of the Invention] In this invention, as explained above, application to an optical element etc. can be performed as a functional device by being able to obtain the silica meso structure thin film by which patterning was carried out to the arbitration configuration in the arbitration location which has uniaxial orientation nature in the direction of arbitration by combining the mask rubbing method and a lithography technique, and creating to coincidence the thin film which has uniaxial orientation nature in the direction of arbitration.

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## TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] However, in order to have applied to the functional device in addition to this, the technique which forms an optical element, such as performing polarization control of photoluminescence as hosts, such as a conductive polymer, using the meso porous structure with uniaxial orientation nature, and the meso porous structure thin film to which the direction of meso pore was equal in an arbitration configuration in the direction of arbitration is important for the location of the arbitration on a substrate, and the following troubles were in the Prior art in it.
[0006] By the approach of depositing on substrates, such as Si (110), the substrate dependency of the film formed is large, and is restricted to the substrate with the order nature in atomic level, and a problem is in the arbitration controllability of the direction of meso pore within the same substrate further. Moreover, by the approach of carrying out patterning of the silica meso structure easily using software lithography, a silica meso structure thin film with uniaxial orientation nature cannot be created.
[0007] And by the formation approach with the pore structure of the uniaxial orientation nature by the magnetic field of the meso porous structure, in order to generate a strong magnetic field, equipment became large-scale, and the problem was in the limit to the magnitude of a substrate, or the formation in the location of arbitration. Furthermore, by the formation approach of the meso porous structure which has uniaxial orientation nature using a micro capillary, production of a thin film patterning was carried out [ production ] to the configuration of arbitration by use of a micro capillary was difficult, and there was a trouble that a creation process was still more complicated.
[0008] For this reason, the uniaxial orientation nature of this thin film by which carried out patterning of the silica meso structure thin film which has uniaxial orientation nature to the configuration of arbitration on the substrate of arbitration to the application to the functional device of a silica meso structure thin film, and patterning was carried out separately was wanted to control in the direction of arbitration.
[0009] This invention was made in view of the above-mentioned trouble, and offers the silica meso structure thin film, the meso porous silica thin film, and its manufacture approach of a configuration of the arbitration which has the pore structure of uniaxial orientation nature in the direction of arbitration in the location of the arbitration on a substrate.

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MEANS

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[Means for Solving the Problem] Namely, invention of the first of this invention is a silica meso structure thin film arranged in the location of the arbitration on the high-molecular-compound thin film formed on the substrate. While the direction of orientation of the pore of the shape of tubing in this thin film is equal to 1 shaft orientations, patterning of this thin film is carried out to the desired configuration. And it is the silica meso structure thin film which has the pore structure of the uniaxial orientation nature characterized by the directions of orientation of the pore of at least one or more fields of two or more fields of this thin film by which patterning was carried out differing and by which patterning was carried out.
[0011] Invention of the second of this invention is a meso porous silica thin film which has the pore structure of the uniaxial orientation nature characterized by removing the surfactant in pore from the above-mentioned silica meso structure thin film and by which patterning was carried out.
[0012] The process at which invention of the third of this invention forms a high-molecular-compound thin film in a substrate front face, The process which gives the orientation restraining force of the direction of arbitration to two or more fields of the arbitration of this high-molecular-compound thin film using the mask rubbing method, The process which creates the thin film of the silica meso structure by which said substrate which performed rubbing processing was held in the acid surfactant water solution containing a silicon alkoxide, and the direction of pore was controlled on this substrate, It is the manufacture approach of the silica meso structure thin film by which patterning was carried out of having the pore structure of the uniaxial orientation nature characterized by including the process which fabricates this silica meso structure thin film in the configuration of arbitration with ultra-fine processing technology in the location of the arbitration on a substrate.
[0013] The process at which invention of the fourth of this invention forms a high-molecular-compound thin film in a substrate front face, The process which gives the orientation restraining force of the direction of arbitration to two or more fields of the arbitration of this high-molecular-compound thin film using the mask rubbing method, The process which creates the thin film of the silica meso structure by which said substrate which performed rubbing processing was held in the acid surfactant water solution containing a silicon alkoxide, and the direction of pore was controlled on this substrate, The process which fabricates this silica meso structure thin film in the configuration of arbitration with ultra-fine processing technology in the location of the arbitration on a substrate, It is the manufacture approach of the meso porous silica thin film by which patterning was carried out of having the pore structure of the uniaxial orientation nature characterized by including the process which removes a surfactant out of the silica meso structure thin film formed on the substrate.
[0014] Invention of the fifth of this invention is a meso porous silica thin film which has the pore structure of uniaxial orientation nature which is different to the field to which each other is adjoined on a substrate and by which patterning was carried out, and is the polarization modulation element which can generate the polarization modulated by vibration of the optical exposure and substrate using this thin film that introduced the molecule which emits light by excitation by optical exposure into this pore structure.
[0015]
[Embodiment of the Invention] The silica meso structure thin film of this invention is a silica meso structure thin film arranged in the location of the arbitration on the high-molecular-compound thin film

formed on the substrate. The direction of orientation of the pore of the shape of tubing in this thin film is the silica meso structure thin film which is equal to 1 shaft orientations. It is the silica meso structure thin film which has the pore structure of the uniaxial orientation nature characterized by the directions of orientation of the pore of at least one or more fields of two or more fields of this thin film by which patterning of this thin film is furthermore carried out to the desired configuration, and patterning was carried out differing.

[0016] Moreover, the manufacture approach of the silica meso structure thin film of this invention The process which forms a high molecular compound thin film in a substrate front face, and the process which uses the mask rubbing method for grant of the stacking tendency of this high molecular compound thin film, and gives the stacking tendency of arbitration to two or more fields of arbitration, The process which holds in the acid surfactant water solution containing a silicon alkoxide, and creates the thin film of the silica meso structure on this substrate, This silica meso structure thin film with ultra-fine processing technology, such as a lithography technique or a focusing ion beam machining technique, the location of the arbitration on a substrate, It is the manufacture approach of the silica meso structure thin film by which patterning was carried out characterized by including the process fabricated in the configuration of arbitration of having the pore of uniaxial orientation nature.

[0017] Furthermore by this invention, the meso porous silica thin film which has the pore structure of uniaxial orientation nature and by which patterning was carried out can be obtained by removing the surfactant in the pore of the above-mentioned silica meso structure thin film and the silica meso structure thin film created by the above-mentioned approach by baking or the extract by the organic solvent.

[0018] Below, an embodiment is explained. The reaction container used for formation of the silica meso structure thin film of this invention is the thing of a configuration like drawing 1 . If the quality of the material of a reaction container has the resistance over a chemical, especially an acid, there is especially no limitation and it can use a thing like polypropylene or Teflon (trademark). Into the reaction container, the substrate electrode holder 13 of the acid-proof quality of the material is placed like drawing 1 , and a substrate 15 is held using this. Although drawing 1 has shown the example which holds a substrate horizontally, maintenance of a substrate is not limited horizontally.

[0019] Moreover, although it is common to hold in the reaction solution 22 like drawing 2 (A) as for the substrate 23, also when the near front face where orientation processing of a substrate 23 was performed like drawing 2 (B) is held so that the front face of the reaction solution 22 may be touched, it can form the same thin film. Moreover, when covering 25 is used through a spacer 24 in order to protect the front face of a substrate from the convection current during a reaction as shown in drawing 2 (C), there is an inclination for the homogeneity of the meso porous silica thin film formed to improve. A reaction container may be put into the well-closed container of the rigid high quality of the material still like stainless steel so that it may not be destroyed, even if a pressure is applied during a reaction.

[0020] In this drawing, a reaction solution mixes acids, such as a hydrochloric acid, in a surfactant water solution, and it is SiO2. To what was adjusted to less than [ pH=2 ] which is the isoelectric point, the alkoxide of silicon like a tetra-ethoxy silane is mixed. A surface active agent is suitably chosen from a cationic surface active agent like the 4th class alkylammonium, alkylamine, a nonionic surfactant like polyethylene oxide, etc. The die length of the surfactant molecule to be used is decided according to the pore size of the target meso structure. Moreover, in order to enlarge the path of a surface-active-agent micell, an additive like a mesitylene may be added. The high molecular compound thin film is formed in the front face, and what performed rubbing processing to this further is used for a substrate. Although there is especially no limitation in the quality of the material of the substrate which forms a high-molecular-compound thin film, a stable thing is desirable to acid conditions. If it illustrates, quartz glass, ceramics, resin, etc. are usable. Generally rubbing processing is well used as technique for carrying out orientation of the liquid crystal on the substrate, coating of a polymer is performed on a substrate by the technique of a spin coat etc., and the approach of carrying out rubbing of this with cloth is mainly used. Usually, the rubbing cloth is twisted around the roller, contacts the rotating roller on a substrate front face, and performs rubbing.

[0021] In this invention, in order to give uniaxial orientation nature to the silica meso structure thin film of two or more fields by which patterning was carried out in the direction of arbitration, multiplex rubbing by the mask rubbing method is performed for the purpose of the arbitration location to the high

molecular compound film, and grant of an arbitration stacking tendency. A fundamental process is the same as that of the case where the substrate to which orientation of the common liquid crystal is carried out is created, the rubbing processing to the high molecular compound film and mask formation are repeated, finally a mask is removed, and the resist pattern formed with the lithography technique is used for a mask.

[0022] As an example of multiplex rubbing by the mask rubbing method, the approach of stacking tendency grant of a direction which is different in two fields on the high-molecular-compound film on a substrate is explained. First, rubbing processing is carried out and the stacking tendency X of the 1st direction is given towards a request on the whole substrate surface which formed the high molecular compound film like drawing 3 (a). Next, a resist pattern is formed with a lithography technique as a mask of a part to save the stacking tendency of the 1st direction like drawing 3 (b). And the still more nearly same rubbing processing as desired another direction is performed like drawing 3 (c), and the stacking tendency Y of the 2nd direction is given. At this time, the stacking tendency which gave the part in which a mask is not carried out by the resist in the 1st direction is lost, and the stacking tendency by rubbing processing of the 2nd direction is given. It is possible to form two fields where stacking tendencies differ like drawing 3 (d) by removing the resist pattern finally used as a mask. And the silica meso structure thin film which has different uniaxial orientation nature like drawing 3 (e) by the approach explained below can be created.

[0023] What contains two or more continuous methylene groups in the repeat structural unit is used for the high molecular compound thin film formed in a front face. When the number of the methylene groups in a repeat structural unit is 20 or less [ 2 or more ], the good silica meso structure thin film of especially uniaxial orientation nature is obtained, in becoming large more than it, there is an inclination for uniaxial orientation nature to fall, and it is thought that this is because the stacking tendency of the macromolecule given by rubbing will be lost when reaction temperature is raised at the time of a deposit of the silica meso structure thin film described below.

[0024] The meso structure of a silica can be deposited on a substrate on such conditions. There is especially no constraint in the temperature at the time of making it deposit, and it is chosen as it in an about [ room temperature -100 degree C ] temperature field. As for reaction time, such film with it is formed in several hours - about several months that time amount is short. [ thin ] And after pure water washes the film which carried out in this way and was formed on the substrate, it is made to season naturally in air, and a silica meso structure thin film is obtained.

[0025] A meso porous silica thin film can be created by removing the surfactant micell of a template from this silica meso complex. Baking, the extract by the solvent, etc. are used for removal of a surfactant. For example, a surfactant can be completely removed from a meso structure thin film by calcinating at 550 degrees C for 10 hours among air, without destroying most of meso structure and its uniaxial orientation nature. Moreover, if solvent extraction is used, although removal of 100% of surfactant is difficult, it is possible to form a meso porous thin film on the substrate of the quality of the material which cannot bear baking.

[0026] Thus, it is possible to carry out patterning of the silica meso structure thin film and meso porous silica thin film which have the created uniaxial orientation nature with light, an X-ray, an electron ray, the lithography technique using an ion beam, and focused ion beam (FIB) processing techniques, such as UV. Although some processes are required of the approach using a lithography technique, it is effective in patterning of a field large at once, and although patterning of the large field cannot be carried out at once by FIB processing on the other hand compared with micro processing by the lithography technique, patterning is easily possible, without needing a complicated process.

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[Translation done.]

## EXAMPLE

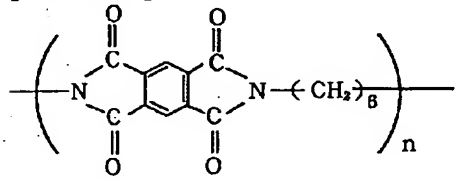
[Example] Although this invention is hereafter explained to a detail using an example, this invention is not limited to an example and an ingredient, a reaction condition, etc. can be freely changed in the range in which the silica meso structure thin film of the same structure is obtained. Moreover, it is not limited to the example explained below about the pattern formation of a silica meso structure thin film and a meso porous silica thin film, and arbitration stacking tendency grant.

[0028] In example 1 this example, it is an example which formed in the location of arbitration the meso porous silica thin film by which patterning was carried out to the configuration of arbitration, and applied this to the optical element with formation of the silica meso structure thin film which has uniaxial orientation nature in the different direction, and the detailed technique by the photolithography by performing the arbitration location to the high-molecular-compound thin film formed on the substrate by the mask rubbing method, and stacking tendency grant of the direction of arbitration. This is explained using drawing 4 - drawing 9 .

[0029] On the quartz-glass substrate of 20mm angle, the NMP solution of polyamic acid A which is a precursor was applied with the spin coat, it calcinated at 200 degrees C for 1 hour, and the thin film of the polyimide A which has the following structures was formed.

[0030]

[Formula 1]



ポリイミドA

[0031]

[Table 1]

表 1　　ポリイミドAのラビング条件

| 布材質 | ナイロン |
|---|---|
| ローラー径 （ mm ） | 24 |
| 押し込み （ mm ） | 0.4 |
| 回転数 （ rpm ） | 1000 |
| ステージ速度 （ mm／min ） | 600 |
| 繰り返し回転 | 2 |

[0032] On the other hand, the substrate which performed mask rubbing processing was created. First, as shown in drawing 4 (a), after performing rubbing processing of the 1st direction to the whole substrate 41 on condition that Table 1, negative resist 43 was applied all over the substrate, and the resist pattern

of the shape of a stripe with a width of face [ of a direction perpendicular to the 1st direction ] of 2mm was formed at intervals of 2mm by mask exposure and the development on the substrate to leave the effectiveness of rubbing of the direction X of the 1st like drawing 4 (b). In addition, the side face of the resist pattern used as a mask was created on the conditions which do not become inverse tapered shape-like.

[0033] Next, as shown in drawing 4 (c), rubbing processing on the same conditions as rubbing processing of the 1st direction was performed in the perpendicular direction to the 1st direction. In addition, in rubbing processing of the direction Y of the 2nd to the part which does not form the resist pattern, the rubbing effectiveness of the 1st direction will be lost and the rubbing effectiveness of the 2nd direction will be given. And by removing the resist pattern formed as a mask of mask rubbing processing, as shown in drawing 4 (d), the substrate which gave orientation restraining force to the polyimide A on a quartz-glass substrate in two or more locations of arbitration was created, and this was made into the substrate for depositing a silica meso structure thin film.

[0034] The reaction solution dissolved 2.82g of cetyl trimethylammonium chlorides in 108ml pure water first, added 48.1ml of hydrochloric acids 36%, stirred them for 2 hours, and was used as the acidic solution of a surfactant. And tetra-ethoxy silane (TEOS) 1.78ml was added to this solution, and it stirred for 2 minutes and 30 seconds, and created.

[0035] The above-mentioned substrate was put into the substrate holder for the substrate maintenance in the Teflon container of the configuration of drawing 1 , the substrate was held in the solution, and the silica meso structure which has the uniaxial orientation nature corresponding to the direction of rubbing which went to the arbitration location on a substrate like drawing 4 (e) was deposited. The front face of a substrate is covered with covering of quartz glass through a spacer with a thickness of about 0.2mm, and it was made for a bad influence not to reach [ the effect of the convection current ] orientation. A final solution presentation is a mole ratio and is H2 O=100:HCl=7:cetyl trimethylammonium chloride =0.11:TEOS=0.10. This container was covered, and after putting into the well-closed container of further the product made from stainless steel, it held in the oven kept at 80 degrees C. The holding time was made into 48 hours.

[0036] After it picked out the substrate contacted in the predetermined time amount reaction solution from a container and pure water fully washed, this substrate was dried in air. When the substrate front face was observed with the optical microscope, the texture corresponding to each rubbing direction was seen. Furthermore, it was checked that the meso channel which had uniaxial orientation nature in the perpendicular direction to the direction of rubbing about the silica meso structure thin film of each field where rubbing processings differ when the cross-section TEM image by the 100kV electron ray was observed is formed. It was checked that the silica meso structure thin film from which the direction of orientation of the pore structure which has uniaxial orientation nature like drawing 5 (a) differs by the field is formed in the whole surface. Furthermore, it was also checked that the meso channel forms hexagonal structure uniformly from a quartz-glass substrate to a front face.

[0037] Thus, the photolithography performed patterning like drawing 5 (b) for the silica meso structure thin film with the uniaxial orientation nature formed on the substrate. By patterning, the direction of orientation of pore structure with uniaxial orientation nature created the field where two mutually different area is equal. First, mask exposure by UV light was performed into the part to leave this thin film after applying negative resist to the whole surface of a creation substrate, and the desired resist pattern was formed. Next, this thin film was etched with the buffer solution (NH4 F-HF:pH4.5) of fluoric acid. And after performing pure-water washing, the resist pattern was removed, and the silica meso structure thin film by which patterning was carried out was obtained.

[0038] In order to remove a surfactant out of this silica meso structure thin film by which patterning was carried out, put this thin film by which patterning was carried out into the muffle furnace, and it was made to go up to 550 degrees C with 1-degree-C programming rate for /, and calcinated in air for 10 hours. The surfactant removed by baking and the meso porous silica thin film by which patterning was carried out was obtained.

[0039] The application to an optical element was tried for the silica meso structure thin film created on the substrate as mentioned above. Semi-conductor polymer MEH-PPV (Pori [2-methoxy-5-(2'-ethylhexyloxy)-1 and 4-phenylenevinylene]:poly[2-methoxy-5-(2'-ethylhexyloxy)-1, 4-phenylene vinylene]) was introduced into the pore of the meso porous silica thin film by which patterning was

carried out. Installation of MEH-PPV carried out by dipping this thin film into the chlorobenzene solution which melted MEH-PPV, and obtained the meso porous silica thin film which introduced MEH-PPV by making it dry behind.

[0040] Next, the white light (500mW) was irradiated at each field to two fields to which the directions of orientation of the pore structure of having uniaxial orientation nature differ like drawing 6 (c) and drawing 7 (d), and the reinforcement of polarization of the photoluminescence light from MEH-PPV was measured. In addition, in measurement, in order to suppress dispersion from the structure of a meso porous silica, this thin film was dipped into the mixed solution of glycerol and propanol, and was performed.

[0041] When the direction of a polarizing filter was set in the same direction as the direction of orientation of the meso channel of Field B and the polarization reinforcement of photoluminescence light was measured like drawing 6 (c), as for polarization of the photoluminescence light from Field B, about about 5-time reinforcement was obtained to it of Field A.

[0042] On the other hand, as shown in drawing 7 (d), when the direction of a polarizing filter was set in the same direction as the direction of orientation of the meso channel of Field A and the polarization reinforcement of photoluminescence light was measured, as for polarization of the photoluminescence light from Field A, about about 5-time reinforcement was obtained to it of Field B.

[0043] Then, like drawing 8 (e) and drawing 8 (f), patterning of this thin film was carried out, the substrate was vibrated right and left, and the field which carries out white light incidence was changed. When measured by the case where a polarizing filter parallel to the direction of a meso channel of this thin film of Field A is set for the reinforcement of polarization of the photoluminescence light from MEH-PPV of this thin film of the field A at that time, and Field B, and the case where a polarizing filter parallel to the direction of a meso channel of this thin film of Field B is set, as shown in drawing 9 (g), the polarization with a modulation was acquired and the optical element which can be used as a polarization modulation element was able to be created.

[0044] Example 2 this example is an example which applied this to the optical element similarly using the silica meso structure thin film on the quartz-glass substrate of 20mm angle created under the same conditions as an example 1. It explains using drawing 4 - drawing 9 .

[0045] First, after forming the thin film of Polyimide A on the quartz-glass substrate of 20mm angle, two fields where the rubbing processing directions differ in the polyimide A on a substrate were formed in the same conditions and same process as an example 1, and it considered as the substrate which deposits the silica meso structure thin film which has the pore structure of having uniaxial orientation nature.

[0046] Next, the silica meso structure thin film was formed on this substrate by holding this substrate in a reaction solution on the same conditions as an example 1. After picking out said substrate from a reaction container, and pure water fully washed and making it dry in air, when the substrate front face was observed with the optical microscope, the texture corresponding to each rubbing direction was seen like the example 1. Furthermore, it checked that the meso channel which had uniaxial orientation nature in the perpendicular direction to the direction of rubbing by the same cross-section TEM observation as an example 1 was formed, and checked that the silica meso structure thin film from which the direction of orientation of the pore structure which has uniaxial orientation nature like drawing 5 (a) differs by the field was formed in the whole surface.

[0047] Thus, after cutting down the substrate in which the silica meso structure thin film with uniaxial orientation nature was formed, on 5mm square with a dicing saw, this thin film like drawing 5 (b) by which patterning was carried out was created in 150micrometerx300micrometer magnitude with focused ion beam (FIB) processing equipment. First, it fixed to the sample holder and this substrate cut down on 5mm square with the dicing saw was introduced in the vacuum chamber of FIB processing equipment. Next, the focused ion beam was irradiated to the thin film field to delete, it deleted by carrying out sputtering of said thin film field, and the meso porous silica thin film by which patterning was carried out was obtained.

* NOTICES *



1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

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## DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]
[Drawing 1] In this invention, it is the schematic diagram showing the reaction container for forming a silica meso structure thin film.
[Drawing 2] It is an explanatory view for setting to this invention and explaining the maintenance approach of the substrate in a reaction solution.
[Drawing 3] In this invention, it is the explanatory view for explaining the mask rubbing method given to the high molecular compound formed on the substrate to give.
[Drawing 4] In the example 1 of this invention, it is an explanatory view explaining the creation approach of a meso porous silica thin film with the uniaxial orientation nature which changes to two or more fields with mask rubbing methods.
[Drawing 5] In the example 1 and example 2 of this invention, it is drawing which introduces a semiconductor polymer into a meso porous structure thin film with uniaxial orientation nature which is different to created two or more fields, and explains the application to an optical element.
[Drawing 6] In the example 1 and example 2 of this invention, it is drawing which introduces a semiconductor polymer into a meso porous structure thin film with uniaxial orientation nature which is different to created two or more fields, and explains the application to an optical element.
[Drawing 7] In the example 1 and example 2 of this invention, it is drawing which introduces a semiconductor polymer into a meso porous structure thin film with uniaxial orientation nature which is different to created two or more fields, and explains the application to an optical element.
[Drawing 8] In the example 1 and example 2 of this invention, it is drawing which introduces a semiconductor polymer into a meso porous structure thin film with uniaxial orientation nature which is different to created two or more fields, and explains the application to an optical element.
[Drawing 9] In the example 1 and example 2 of this invention, it is drawing which introduces a semiconductor polymer into a meso porous structure thin film with uniaxial orientation nature which is different to created two or more fields, and explains the application to an optical element.
[Description of Notations]
11 Teflon Container
12 Teflon Lid
13 Substrate Electrode Holder made from Teflon
14 Seal (O Ring)
15 Substrate
21 Reaction Container
22 Reaction Solution
23 Substrate
24 Spacer
25 Covering
31 Quartz-Glass Substrate
32 Orientation Film Which Gave Rubbing
33 Resist
34 Surfactant Rod-like Micell (Perpendicular to Space)
35 Surfactant Rod-like Micell (Parallel to Space)

41 Quartz-Glass Substrate
42 Polyimide A
43 Negative Resist
44 Surfactant Rod-like Micell
51 Silica Meso Structure Thin Film
52 Quartz-Glass Substrate
53a, 53b Polarizing filter
54 Detector
55 White Light
56 Photoluminescence Light

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[Translation done.]

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DRAWINGS

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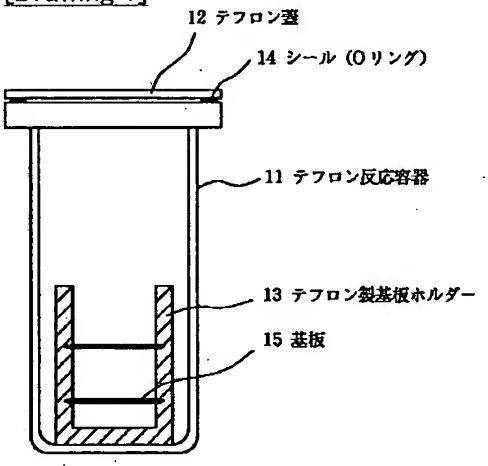
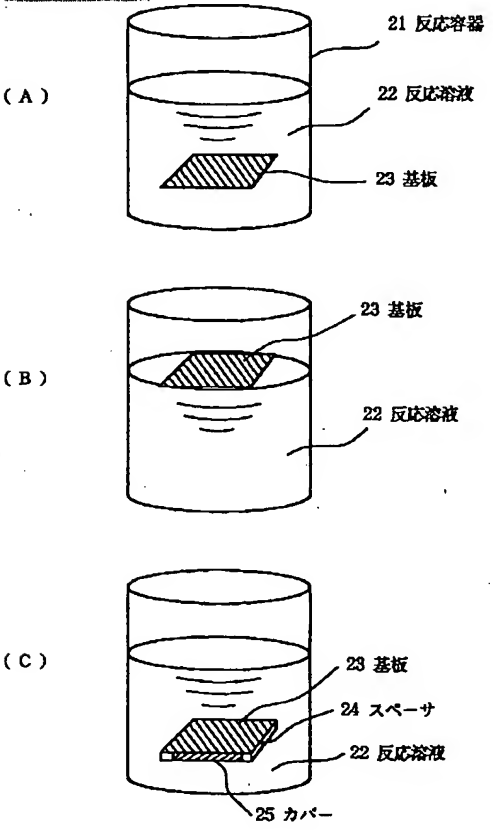
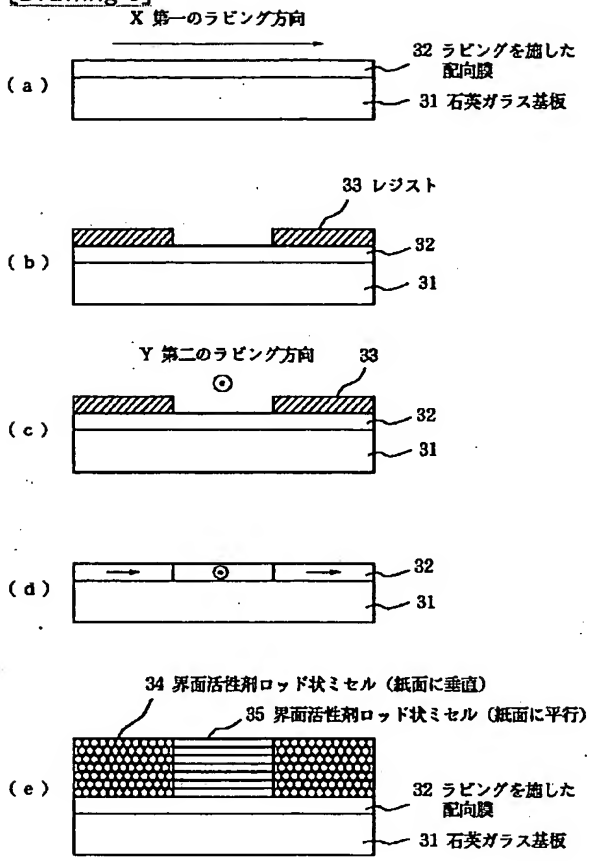
[Drawing 1]



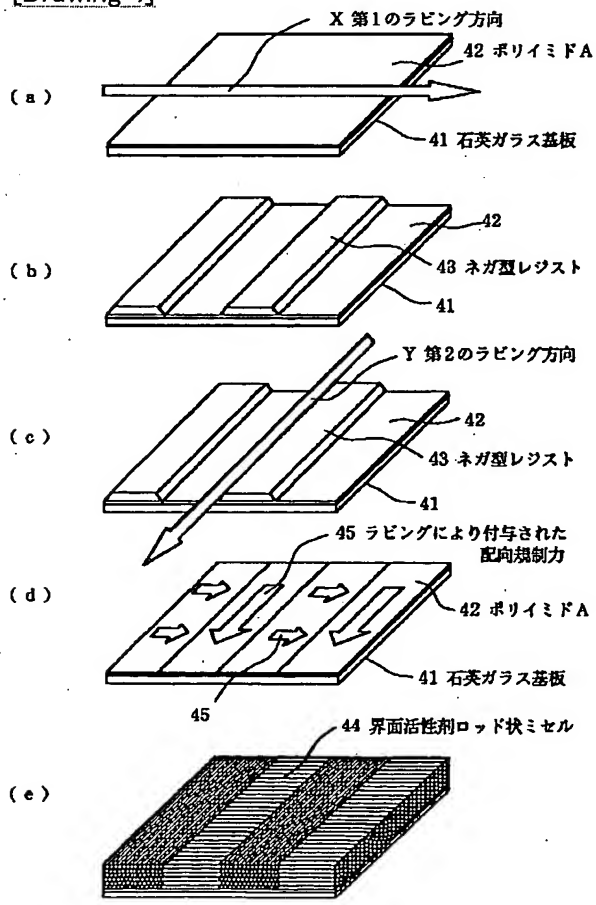

[Drawing 2]



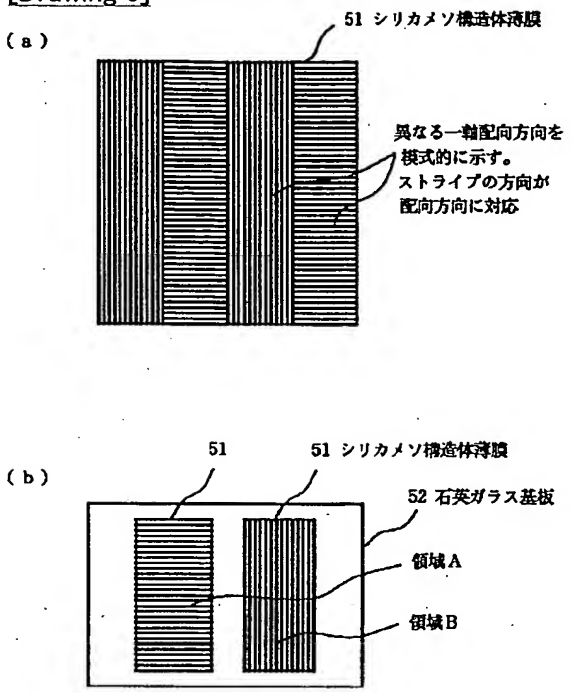
[Drawing 3]




[Drawing 4]

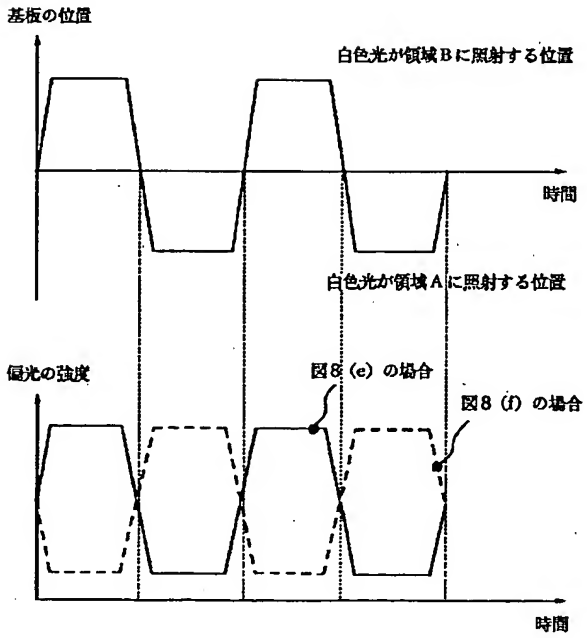


[Drawing 5]

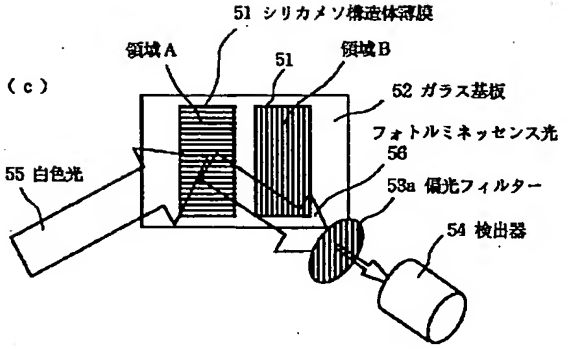


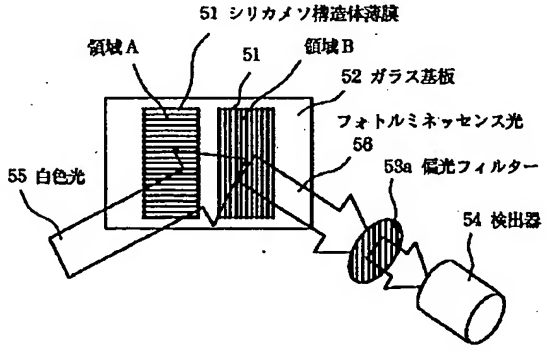

[Drawing 9]

(g)

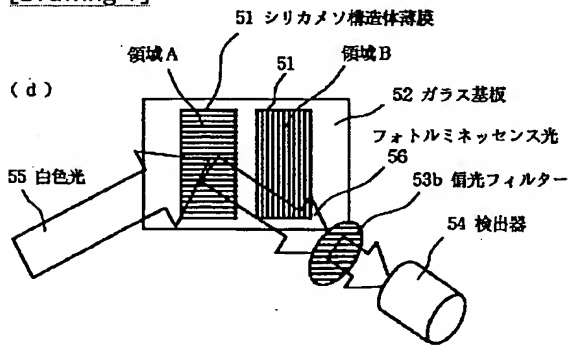


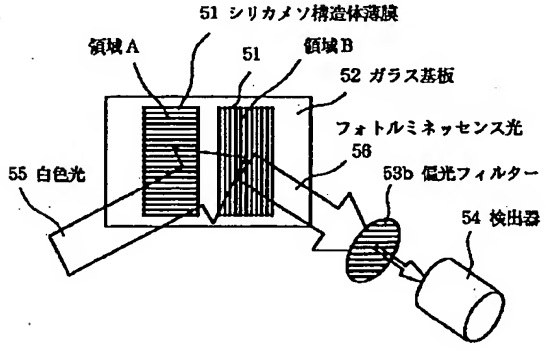

[Drawing 6]



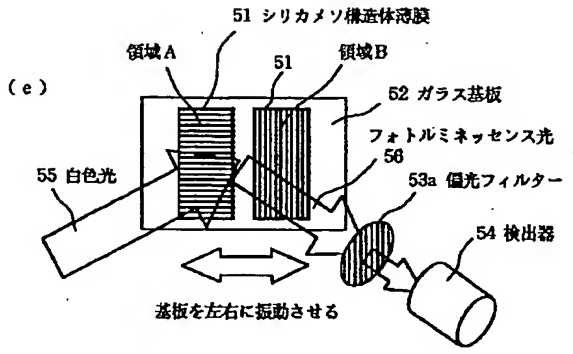



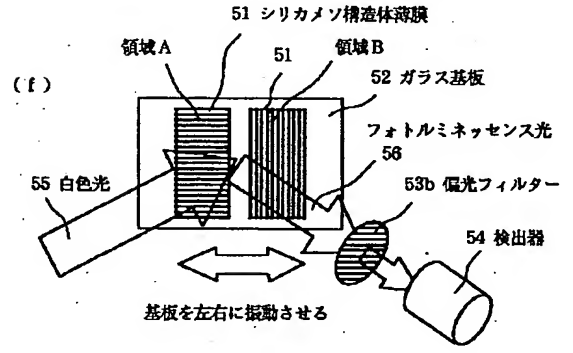

[Drawing 7]




[Drawing 8]

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